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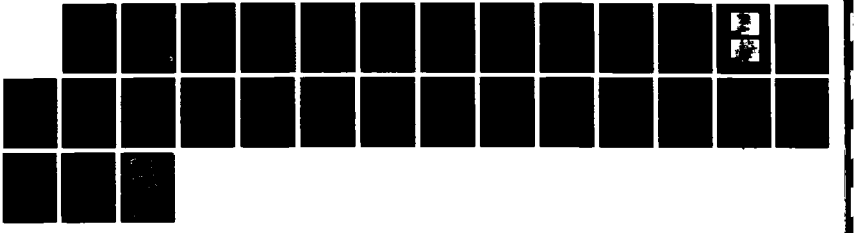

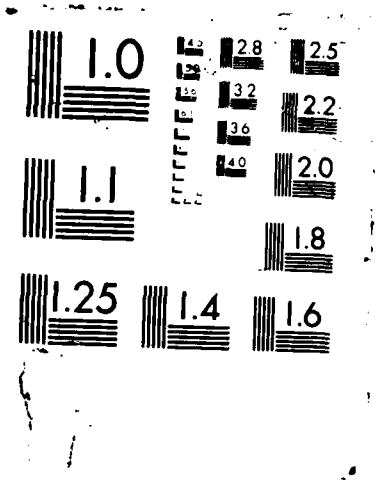
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Work during the present period of the grant has been directed to two principal areas: Microstructure of Epoxy Resins; and Ceramics from Organometallic Polymers. The former area of research was substantially completed during the present year; and future attention will be focussed on the chemical and kinetic aspects of wet chemical processing of ceramic materials.

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FINAL REPORT

ON

MICROSTRUCTURE OF CERAMICS DERIVED FROM ORGANO-METALLIC POLYMERS

submitted to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

by

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

(AFOSR-85-0026)

Professor D.R. Uhlmann

March 1, 1986

I. INTRODUCTION

Work during the present period of the grant has been directed to two principal areas: Microstructure of Epoxy Resins; and Ceramics from Organometallic Polymers. The former area of research was substantially completed during the present year; and future attention will be focussed on the chemical and kinetic aspects of wet chemical processing of ceramic materials.

Progress in each of these areas will be summarized below.

II. MICROSTRUCTURE OF EPOXY RESINS

The present work represented a continuation of our efforts directed to understanding the microstructure of epoxy resin cured with amine hardeners. The focus has been on characterizing a series of networks formed by changing the formulations and the processing conditions of the system. The morphological analysis has been supplemented by a statistical model for the network formation; and the results have been used to understand and control the mechanical properties of these materials.

The table on the following page shows the Epon 828 epoxy/triethylene tetramine (TETA) formulations which were explored, together with the curing conditions employed.

Figure 1 shows the glass transition temperatures (T_g) of these specimens. Table 2 shows the molecular weight between the crosslinks (M_c) for some of the formulations. M_c was evaluated from the rubbery modulus of the resins after applying rubber elasticity theory. The epoxy-rich formulations have higher M_c, which decreases towards the stoichiometric formulations, and then again increases with increasing curing agent concentration. M_c decreased after the post curing treatment. A relationship has been found between T_g and M_c:

$$T_g = 51.7 + 23800/M_c \qquad (1)$$

The modulus at room temperature of these resins is shown in Figure 2. The modulus decreases with increasing hardener content, especially around stoichiometry. From the published literature, epoxies have been assigned a two phase structure (nodular) from an analysis of their fracture surfaces and dynamic mechanical properties. The dispersed phase accounts for more

TABLE 1

EPON/TETA Formulations

Condition	Concentration of Curing Agent, PHR	Epoxide/Amine Hydrogen (E/A)	Curing Condition* hour , C
A	6.5	2:1	7,120
B	6.5	2:1	4 RT/7,120
C	8	1.63:1	4 RT/7,120
E	10	1.3:1	7,120
F	10	1.3:1	4 RT/3,83
G	10	1.3:1	4 RT/8,83
H	12	1.06:1	1 RT/8,83
I1	13	1:1	7,110
I2	13	1:1	7,110
K1	13	1:1	8,83
K2	13	1:1	8,83
L1	13	1:1	1 RT/8,83
L2	13	1:1	1 RT/8,83
M	17	1:1.3	12,80
N	17	1:1.3	3 RT/9,80
Q	26	1:2	12,80
R	26	1:2	3 RT/9,80

*RT is Room Temperature.

A part of each of the samples was also subjected to Postcure at 150 C for two hours. This will be indicated in the text by a superscript P.

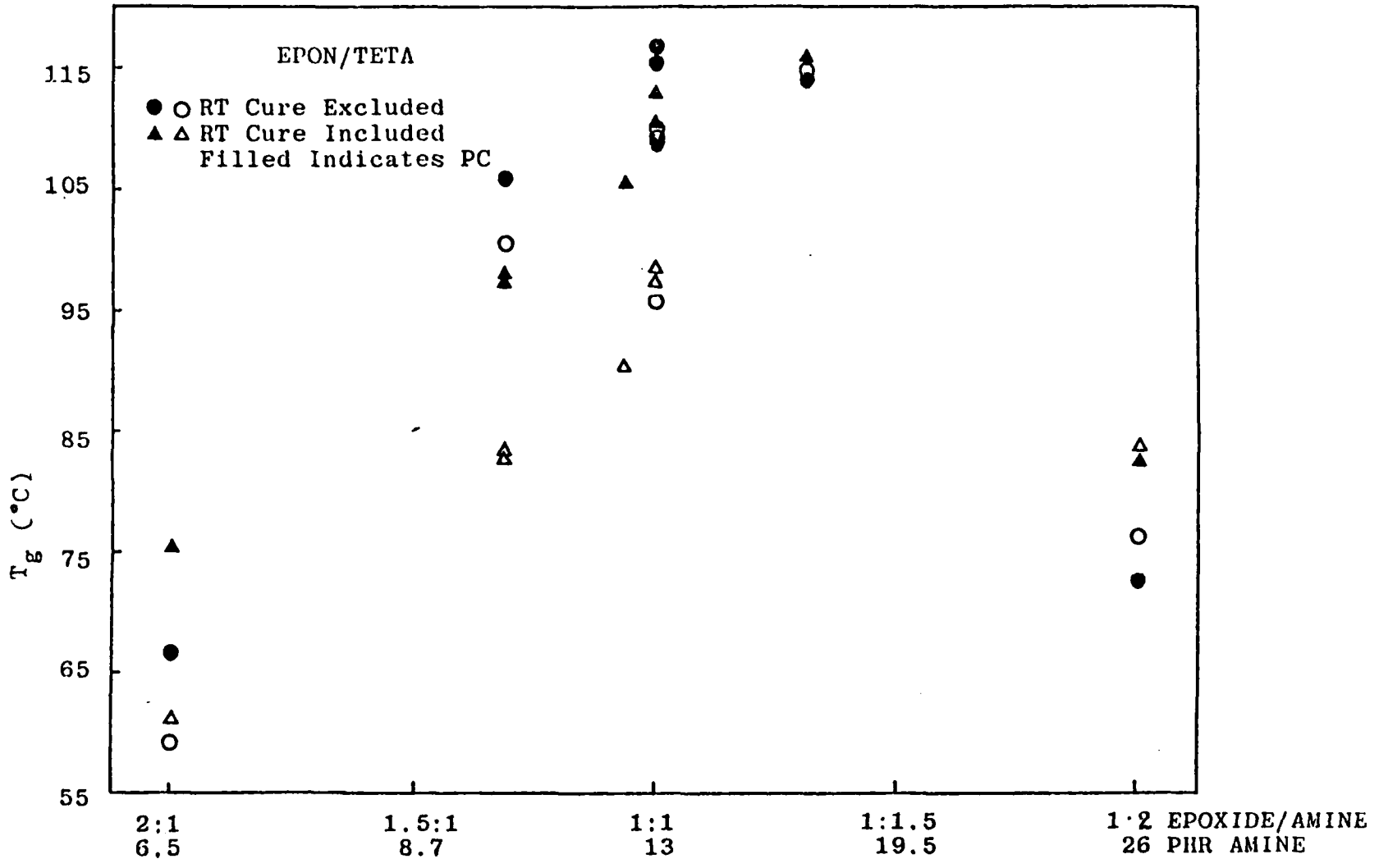

EPON/TETA
● ○ RT Cure Excluded
▲ △ RT Cure Included
Filled Indicates PC
115
105
95
85
75
65
55
T_g (°C)
2:1
6.5
1.5:1
8.7
1:1
13
1:1.5
19.5
1·2 EPOXIDE/AMINE
26 PHR AMINE

Figure 1

TABLE 2

Condition	M_c (grs/mole)
A	2059
K1	580
I2	408
R	905
A^P	1528
$K1^P$	393

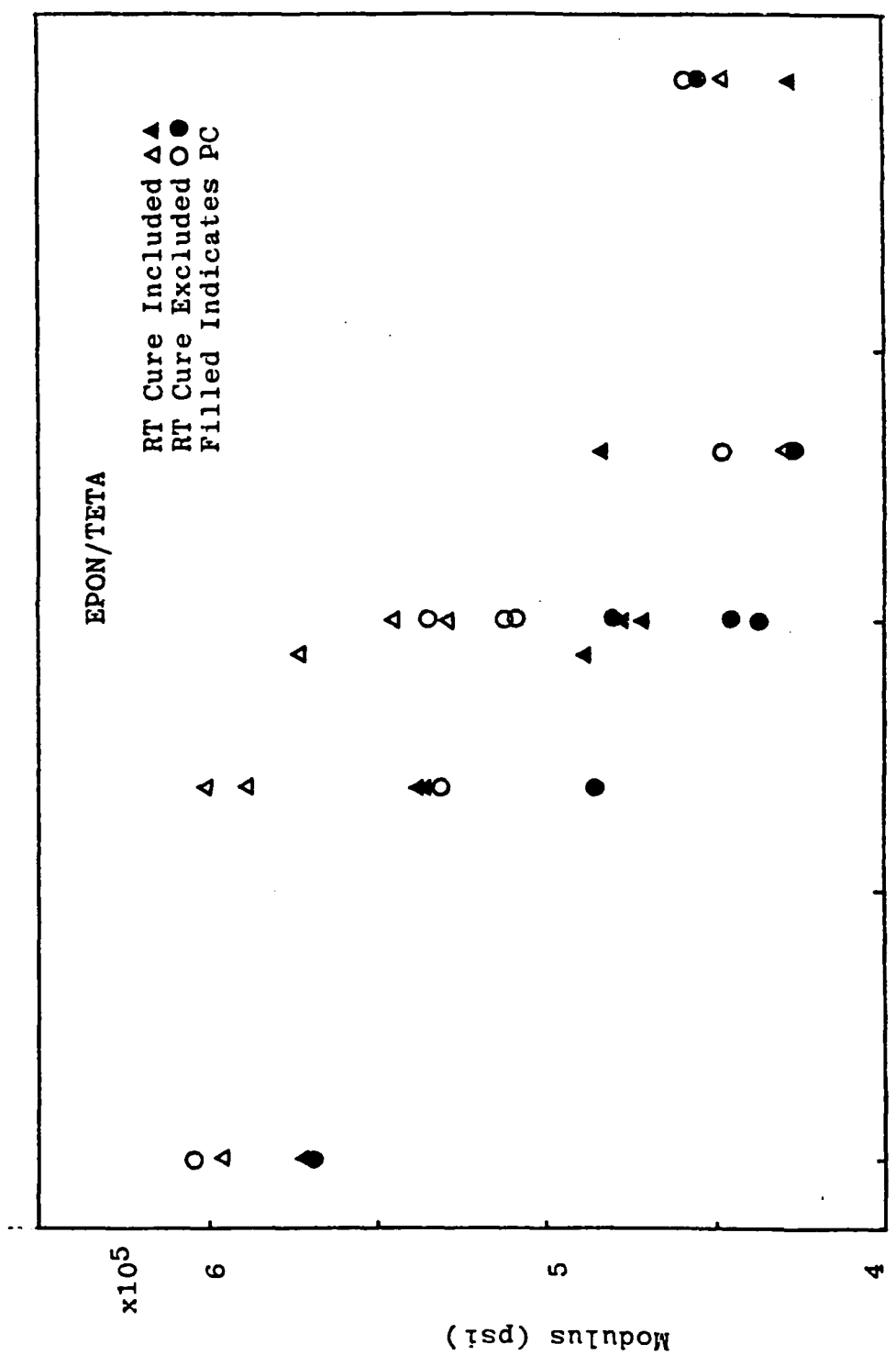


Figure 2 - Flexure modulus (from 4 point bend method) plotted against stoichiometry.

than 50 volume % with an average nodule size of 200-300 Å. The nodules are assumed to be rich in amine and thus have a higher crosslink density than the matrix. This increases their hardness and makes them undeformable.

Figure 2 clearly shows, however, that amine-rich formulations have lower modulus than epoxy-rich or stoichiometric compositions. Hence the arguments based on the occurrence and characteristics of nodules are inconsistent with the data. It has also been shown by SAXS studies that if nodules did exist in the sizes and volume fractions claimed above, then the density difference between the matrix and nodules would be less than 0.1%.

Figure 3 shows a crossplot of the T_g vs modulus data. At both the ends of the curve, T_g drops without a change in modulus. On the left hand side of the figure, the drop occurs for materials which are amine rich (conditions Q, R, Q^P, R^P) and at the other end for the epoxy rich materials (A, B, A^P, B^P). This drop cannot be taken as the formation of the second phase, because if this happened then the modulus would change at constant T_g.

This phenomenon can be explained by a plasticization effect. In the epoxy-rich region, unreacted epoxide plasticizes the matrix; and in the amine-rich region, the high concentration of the flexible curing agent gives the same effect. STEM observations (under Z contrast) on microtomed and stained sections of these specimens show a heterogeneous nature (Figure 4). These were observed only for amine rich formulations, or for stoichiometric compositions which were precured at room temperature. DSC and DMA do not show the presence of two T_g's or shoulders in Tan δ around T_g.

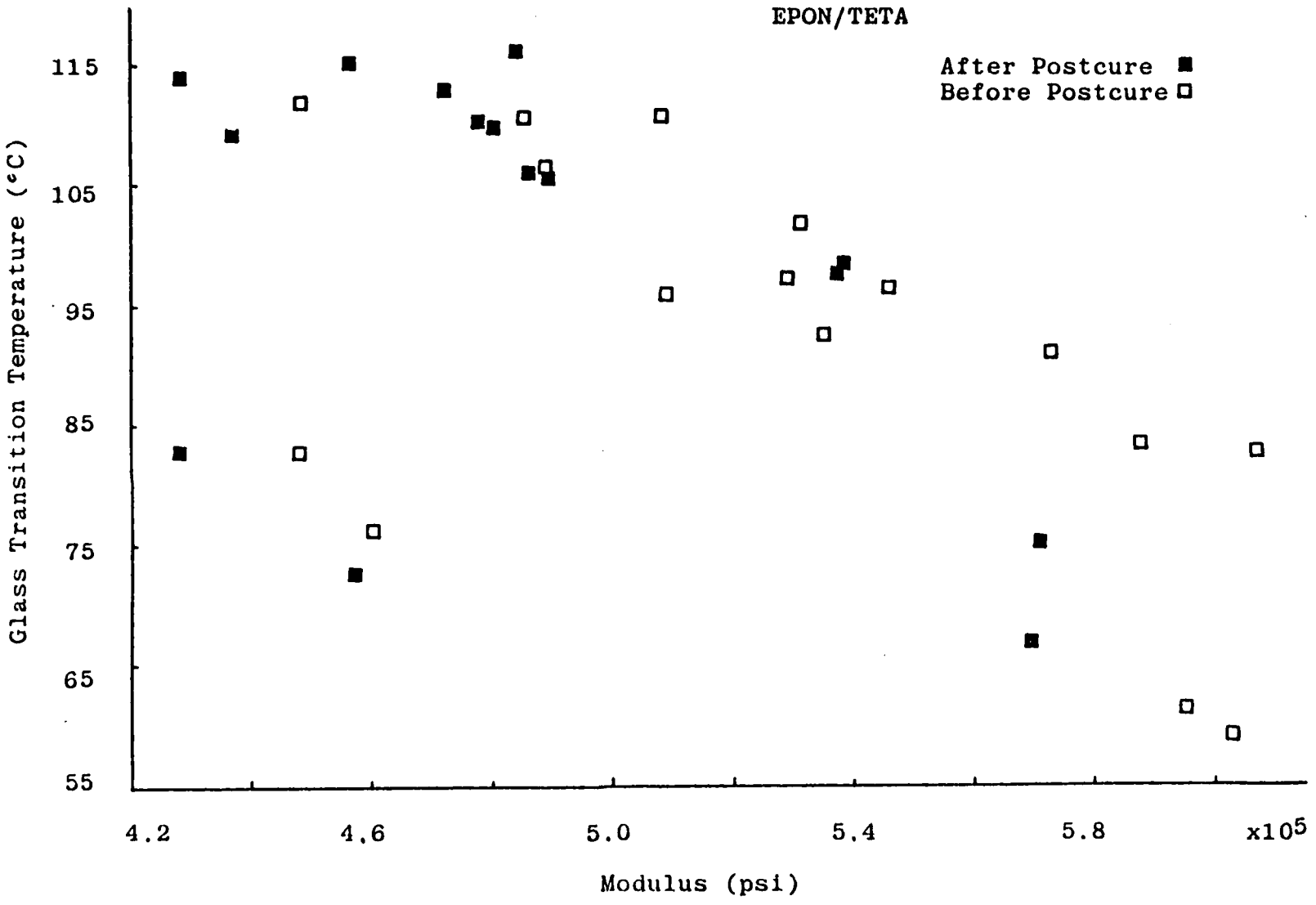
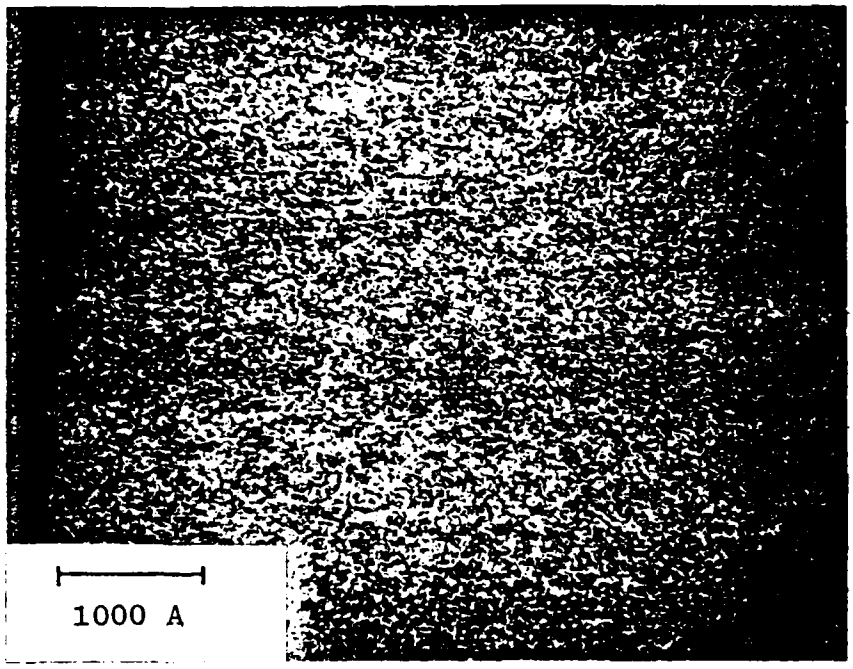
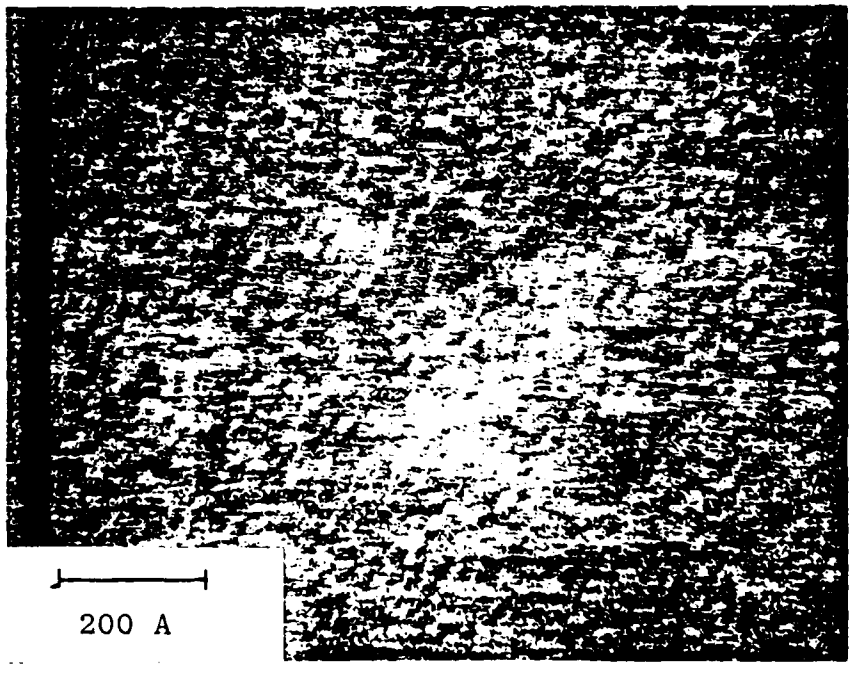


Figure 3 -Onset of Glass Transition Temperature from DSC vs Flexure Modulus.



(a)



(b)

Figure 4 - Stained STEM micrographs for stoichiometric (condition $L2^P$) formulation. Room temperature cure was given.

It has previously been observed in an aromatic amine/DGEBA epoxy system that the reactivity ratio of the primary and secondary amine (K_1/K_2) is around 5. If this were the case in the present system, then in an amine rich system the primary H will react with the epoxies tending to form long linear chains, which could then precipitate out of the epoxy-rich matrix creating a two-phase system.

It was decided therefore to model the growth of a system with a varying K_1/K_2 and stoichiometry to obtain insight into the types of species formed at various stages of reaction. Figure 5 show the fractions of primary (Q1) amine reacted for different stoichiometries and reactivity ratio r($r=K_1/K_2$) as a function of epoxide consumption. This figure shows the variations only up to the onset of gelation. It should be noted from the figure that the epoxide consumed at the gel point does not vary greatly with changing reactivity ratio.

Table 3 shows the various species that can be generated during the curve of epoxies; and Tables 4 to 9 show the concentrations of the different components at various stages of the reaction. It is seen that at the gel point, in the epoxy rich mixture, most of the contribution to the total extent of reaction comes from highly branched units (N2PIS, N2P2S, N2p3S); whereas in amine-rich mixtures (A/E=2), it comes from the less branched units (N1POS, N1P1S, NOP1S, N2POS). The only branched units contributing substantially to the latter are N2P1S or N1P2S.

With increasing reactivity ratio (K_1/K_2), one observes that in amine rich mixtures the amount of unreacted TETA is reduced and the contribution from N1P2S decreases at the expense of N2P1S (although both have three of their functionalities reacted).

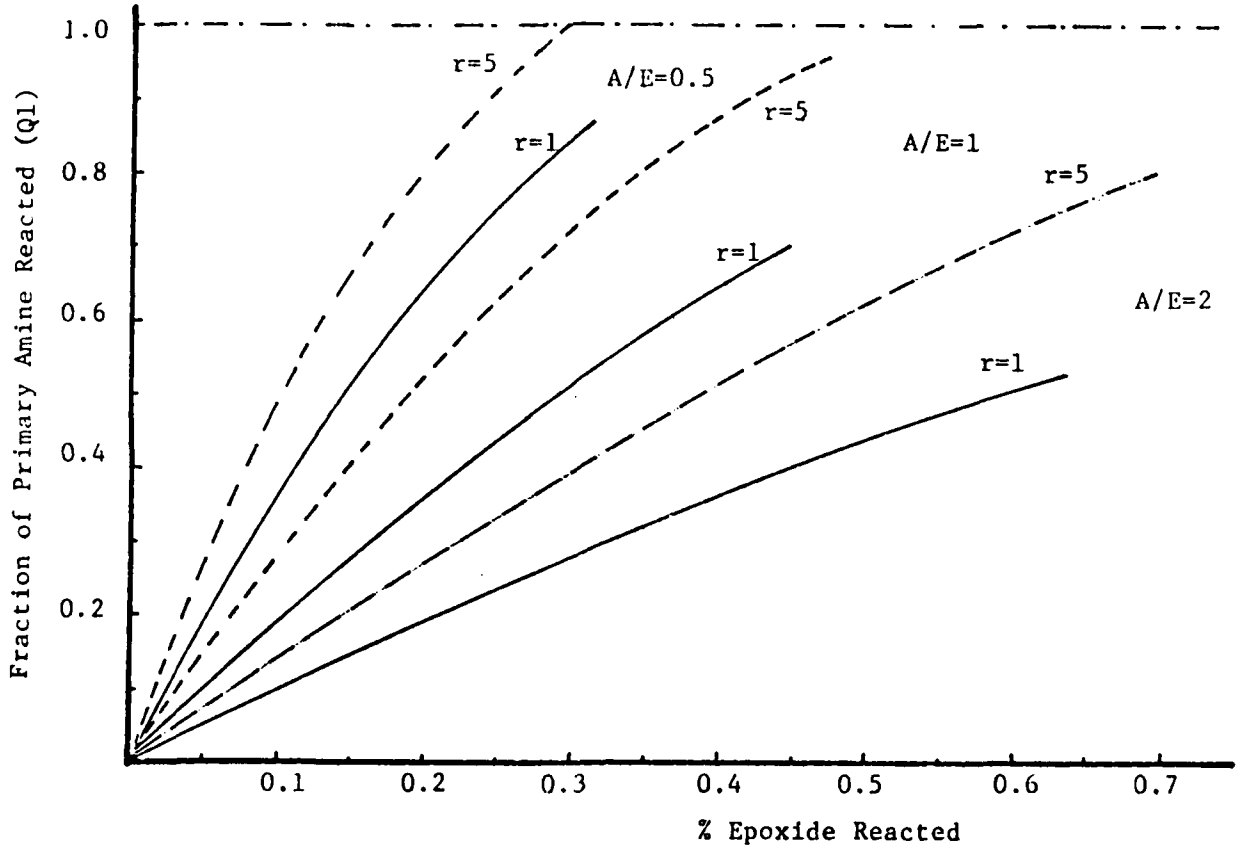
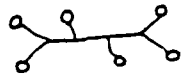
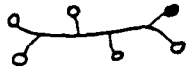
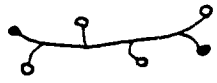
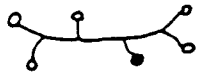
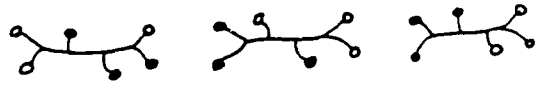
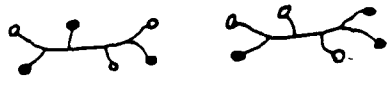
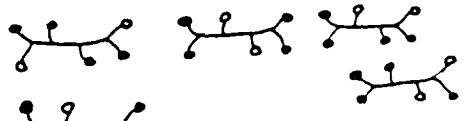
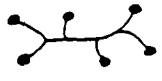


Figure 5 - Fraction of primary amine reacted with increasing consumption of Epoxide. These results are plotted either till gel point or till the primary amine is exhausted.

TABLE 3

Types of Different Species* Generated for TETA.

N0P0S	PSSP	
N1P0S	PSSS	
N2P0S	SSSS	
N0P1S	PSTP	
N0P2S	PTTP	
N1P1S	PSTS, PTSS, TSSP	
N1P2S	PTTS, TSTP, TTSP	
N1P3S	TTTP	
N2P1S	STSS, SSST	
N2P2S	STTS, TSST, TSTS, TTSS	
N2P3S	TTTS, TSTT	
N2P4S	TTTT	

* Specie N0P1S indicates zero primary and one secondary have reacted. This can also be written as PSTP, i.e., the first nitrogen is primary, the second is secondary, the third is tertiary and the last one is also primary. The schematics show TETA molecules, a solid end indicates that it is reacted.

TABLE 4

% of Different Species at Increasing Epoxide Conversion (EPON / TETA)

ρ is the Average Number of Functionalites Reacted for a TETA Molecule

$K_1/K_2 = 1$ AMINE / EPOXIDE = 0.5

Type of Species	% EPOXIDE Conversion		
	8.2	18.4	34.2
N0P0S	34.3	6.4	0.25
N1P0S	26.8	14.9	1.72
N2P0S	5.23	8.65	2.95
N0P1S	13.4	7.44	0.86
N0P2S	1.31	2.16	0.74
N1P1S	13.1	21.6	7.4
N1P2S	2.04	10.05	10.1
N1P3S	0.10	1.46	4.32
N2P1S	3.06	15.1	15.1
N2P2S	0.648	9.49	28.1
N2P3S	0.058	2.54	22.2
N2P4S	0.002	0.247	6.3
ρ =	1.03	2.21	3.79

TABLE 5

% of Different Species at Increasing Epoxide Conversion (EPON / TETA)

ρ is the Average Number of Functionalites Reacted for a TETA Molecule

$K_1/K_2 = 1$ AMINE/EPOXIDE = 1

Type of Species	% EPOXIDE Conversion				
	7.8	16.3	25.8	36.7	44.9
N0P0S	61.4	34.3	16.6	6.4	2.81
N1P0S	20.8	26.8	23.2	14.9	9.14
N2P0S	1.76	5.23	8.1	8.7	7.44
N0P1S	10.4	13.4	11.6	7.43	4.57
N0P2S	0.44	1.31	2.02	2.16	1.86
N1P1S	4.4	13.1	20.2	21.6	18.6
N1P2S	0.3	2.04	5.6	10.05	12.1
N1P3S	0.006	0.10	0.49	1.46	2.46
N2P1S	0.45	3.06	8.4	15.1	18.2
N2P2S	0.041	0.65	3.2	9.49	16.0
N2P3S	0.002	0.058	0.51	2.54	6.01
N2P4S	0	0.002	0.03	0.25	0.82
ρ =	0.47	0.98	1.55	2.21	2.69

TABLE 6

% of Different Species at Increasing Epoxide Conversion (EPON / TETA)

ρ is the Average Number of Functionalites Reacted for a TETA Molecule

$K_1/K_2 = 1$ AMINE/EPOXIDE = 2

Type of Species	% EPOXIDE Conversion						
	7.64	15.6	23.9	32.7	42	62.2	63.2
N0P0S	79.1	61.4	46.5	34.3	16.6	10.72	10.22
N1P0S	12.6	20.8	25.3	26.8	23.2	19.33	18.9
N2P0S	0.5	1.76	3.44	5.23	8.08	8.72	8.74
N0P1S	6.29	10.4	12.7	13.4	11.6	9.67	9.45
N0P2S	0.125	0.44	0.86	1.31	2.02	2.18	2.19
N1P1S	1.25	4.4	8.6	13.1	20.2	21.8	21.9
N1P2S	0.04	0.3	0.94	2.04	5.63	7.86	8.09
N1P3S	0	0.006	0.032	0.10	0.49	0.886	0.935
N2P1S	0.06	0.447	1.4	3.06	8.44	11.8	12.13
N2P2S	0.03	0.041	0.207	0.65	3.19	5.76	6.08
N2P3S	0	0.002	0.013	0.058	0.512	1.20	1.3
N2P4S	0	0	0	0.002	0.03	0.09	0.1
ρ =	0.23	0.47	0.73	0.98	1.55	1.87	1.90

TABLE 7

% of Different Species at Increasing Epoxide Conversion*(EPON / TETA)

ρ is the Average Number of Functionalites Reacted for a TETA Molecule

$K_1/K_2 = 5$ AMINE/EPOXIDE = 0.5

Type of Species	% of EPOXIDE Conversion			
	5.7	12	20.6	29.7
N0P0S	45.6	13.3	0.63	0.001
N1P0S	38.4	37.9	9.7	0.168
N2P0S	8.07	27	37.6	13.37
N0P1S	3.31	2.56	0.33	0.001
N0P2S	0.06	0.122	0.042	0
N1P1S	3.52	9.32	6.66	0.344
N1P2S	0.104	0.74	1.49	0.232
N1P3S	0.001	0.019	0.109	0.032
N2P1S	0.89	8.08	32	34.9
N2P2S	0.036	0.88	10	34
N2P3S	0.001	0.042	1.38	14.6
N2P4S	0	0.001	0.07	2.34
ρ =	0.68	1.45	2.47	3.56

* At 29.7% of Epoxide conversion, all primary amine was exhausted and the Gel point was not reached ($\alpha = 0.84$).

TABLE 8

% of Different Species at Increasing Epoxide Conversion (EPON / TETA)

ρ is the Average Number of Functionalites Reacted for a TETA Molecule

$K_1/K_2 = 5$ AMINE/EPOXIDE = 1

Type of Species	% of EPOXIDE Conversion						
	5.6	11.3	17.4	23.9	31.3	41.1	47.4
N0P0S	69.9	45.6	26.8	13.32	4.74	0.631	0.10
N1P0S	24.5	38.4	42.5	37.9	26.1	9.74	3.5
N2P0S	2.14	8.1	16.8	27	36	37.6	31.1
N0P1S	2.3	3.31	3.31	2.56	1.41	0.33	0.073
N0P2S	0.02	0.06	0.102	0.123	0.105	0.042	0.013
N1P1S	1.01	3.52	6.65	9.32	10.1	6.66	3.48
N1P2S	0.013	0.103	0.34	0.74	1.26	1.49	1.13
N1P3S	0	0.001	0.005	0.019	0.051	0.109	0.121
N2P1S	0.106	0.89	3.19	8.08	17.04	32	38.7
N2P2S	0.002	0.036	0.22	0.884	2.95	10.0	17.9
N2P3S	0	0.001	0.001	0.042	0.222	1.38	3.63
N2P4S	0	0	0	0.001	0.006	0.07	0.273
ρ =	0.34	0.68	1.04	1.44	1.89	2.47	2.84

TABLE 9

% of Different Species at Increasing Epoxide Conversion (EPON / TETA)

ρ is the Average Number of Functionalites Reacted for a TETA Molecule

$K_1/K_2 = 5$ AMINE/EPOXIDE = 2

Type of Species	% EPOXIDE Conversion						
	5.54	11.2	16.9	28.7	41.2	54.9	69
N0P0S	84.2	69.9	57.1	35.6	19.4	8.44	2.73
N1P0S	13.6	24.5	32.7	41.6	41.2	32.8	20.4
N2P0S	0.55	2.14	4.68	12.2	21.9	31.9	38.1
N0P1S	1.32	2.29	2.95	3.4	3.01	2.01	0.97
N0P2S	0.005	0.019	0.038	0.082	0.12	0.119	0.086
N1P1S	0.266	1.01	2.13	5.07	8.12	10.04	9.45
N1P2S	0.002	0.013	0.044	0.199	0.517	0.997	1.43
N1P3S	0	0	0	0.002	0.010	0.032	0.069
N2P1S	0.013	0.11	0.367	1.793	5.23	11.94	21.8
N2P2S	0	0.002	0.010	0.096	0.457	1.64	4.57
N2P3S	0	0	0	0.002	0.017	0.097	0.417
N2P4S	0	0	0	0	0	0.002	0.014
ρ =	0.17	0.34	0.51	0.86	1.24	1.65	2.07

To examine whether such results for large r (>2) in amine-rich systems would lead to the formation of long linear polymer chains (which would then precipitate to give a second phase), further calculations were carried out (see appendix for details of calculations), with the results shown in Tables 10 and 11. These tables lists the % probability for the formation of diads and triads. The type of triad listed is of the type which will lead to longer polymeric species. The probability of the formation of this triad increases appreciably at r = 5 in amine rich formulations. In the limit that r = 2, the reactivity differences between primary and secondary amines will not cause an appreciable change in the nature of the species. However, it may help explain the inhomogeneity of amine rich mixtures.

To consider this, it is useful to evaluate the difference in the solubility parameters required for precipitation. It has been argued that precipitation occurs when Δ is greater than 5

$$\Delta = \sqrt{((\delta_{v1} - \delta_{v2})^2 + (\delta_{h1} - \delta_{h2})^2)} \qquad (2)$$

for polymeric species, and greater than 10 for monomeric species. δ_v and δ_h are the contributions to the solubility parameters due to dispersive polar forces and hydrogen bonding respectively. Subscripts 1 & 2 refer to the precipitating species and the matrix component. Table 12 lists values of these parameters for different species. It can be argued that the polymeric species shown in Table 13 has a Δ of 9.28 (as compared to DGEBA) which is more than 5 hence it would precipitate. The reference point has been taken as DGEBA because only 43% of epoxide had reacted at gelation; therefore an assumption was made that a sea of unreacted epoxy remained.

TABLE 10

Percentage Probability for the Formation of Triads* as the Function of Stoichiometry and K_1/K_2 at different Stages of Reaction

	% Primary Amine Reacted								
	A/E = 2			A/E = 1			A/E = 0.5		
K_1/K_2	15	30	Gel	30%	60%	Gel	30%	60%	Gel
1	8.99	15.64	8.47	7.81	2.71	1.08	3.9	1.36	0.022
2	9.09	19.93	10.4	9.97	6.95	0.94	4.99	3.46	0
5	8.9	22.3	7.12	11.14	11.46	0.12	5.57	5.74	-

* 

TABLE 11

Percentage Probability for the Formation of Diads* as the Function of Stoichiometry and K_1/K_2 at Different Stages of Reaction

	% Primary Amine Reacted								
	A/E = 2			A/E = 1			A/E = 0.5		
K_1/K_2	15	30	Gel	30	60	Gel	30	60	Gel
1	26.3	27.0	10.4	33.6	14.1	7.56	36.9	18.2	1.7
2	24.9	30.2	9.4	35.7	22.5	5.75	38.4	27.2	0.6
5	23.8	32.2	6.64	37.0	30.8	1.9	39.3	35.6	-

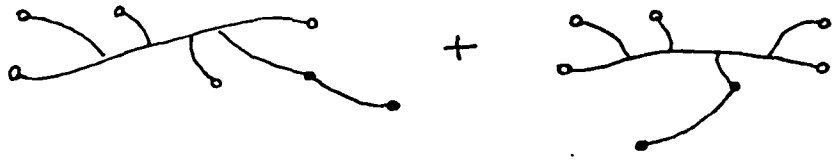
* 

TABLE 12

Solubility* Parameters of Different Species $((J/cm^3)^{1/2})$.

Type of Species	δ_d	δ_p	δ_v	δ_h
Triad	16.44	1.743	16.53	11.61
Primary Diad	17.3	2.04	17.42	10.06
Secondary Diad	17.25	2.60	17.44	10.81
DGEBA	17.21	0.64	17.22	1.72

* $\delta_v = \sqrt{\delta_d^2 + \delta_p^2}$

Subscripts d, p, and h refer respectively to dispersive, polar and hydrogen bonding contributions to the solubility parameter.

TABLE 13

Difference in Solubility* (Δ) for Different Species

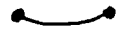
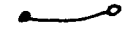
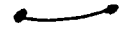
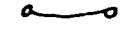
Species 1	Species 2		
	DGEBA	Diad Primary	Diad Secondary
DGEBA	0	8.34	9.09
Diad Secondary	9.09	0.75	0
Diad Primary	8.34	0	0.75
Triad	9.91	1.79	1.21

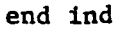
* $\Delta = \sqrt{(\delta_{v1} - \delta_{v2})^2 + (\delta_{h1} - \delta_{h2})^2}$

From a probabilistic calculation, the completely undreacted molecules of epoxide will be only $(1-.43)^2$--i.e., 32%. At gelation (gelation occurs at a different value in amine-rich system here due to a different stoichiometry), completely uncreacted epoxy is present in only a small quantity which cannot form the matrix (Table 14). The matrix consists of diads and other species which have solubility parameters (Tables 12, 13) intermediate between those of unreacted epoxy and the triads (or the higher polymeric species that are formed). Considering one step before gelation, where the phase separation can take place without being hindered sterically, one can consider that the diads (wnich are still soluble in epoxy) act as buffers to keep the triads in solution. The difference in solubility parameter between the epoxy and the triads can be reduced; and it is concluded that phase separation giving rise to a large fraction (50 volume % or more) of heterogeneities cannot be explained in this way.

TABLE 14

Various Kinds of Epoxide Present (%) at Different Stages of Reaction as a Function of Stoichiometry and K_1/K_2

K_1/K_2	Type of Species*	% of Primary Amine Reacted								
		A/E = 2			A/E = 1			A/E = 0.5		
		Gel	30	15	Gel	60	30	Gel	60	30
1		13.5	45.3	71.2	30.4	40	70	46.8	66.6	84
		46.5	44	26.3	49.5	46.5	27.3	43.2	30	15
		40	10.7	2.43	20.1	13.5	2.7	10	34	1.0
2		12.0	53.9	75.9	29.4	50	75.2	46	72.9	87
		45.3	39	22.4	49.6	41.4	23.1	43.6	25	12.4
		42.7	7.1	1.65	21	8.6	1.77	10.3	2.1	0.44
5		9.62	59.7	78.0	27.7	57.9	78.6	-	77.5	89
		42.8	35.1	19.8	49.9	36.4	20.1	-	21.1	10.7
		47.6	52	1.25	22.4	5.73	1.29	-	14.3	0.3

* A solid end indicates reacted.  shows an epoxide molecule with one end reacted.

III. WET CHEMICAL SYNTHESIS OF CERAMICS

Work in this area has been directed to a number of issues. These include: siloxane-modified SiO_2-TiO_2 glasses; crystallization behavior of sol-gel derived glasses; and strengthening of glasses by sol-gel coatings. Progress in each of these areas are summarized in the reprints which appeared in early 1986 and represent work carried out during the present period of the grant.

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